

Engineering Sciences Thermal, Fluid and Aerosciences

Quantum-Kinetic Approach for Modeling Non-Equilibrium Gas-Phase Chemical Reaction Rates

*Progress is being made
in modeling reacting
gas flows under extreme
conditions, such as
vehicle re-entry.*

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In many technologically important areas involving reactive gas flows, including hypersonic reentry, materials processing, and microsystems, the gas is not in thermal equilibrium and cannot be characterized by a single temperature T . Thus, traditional chemistry models based on equilibrium (single-temperature) Arrhenius rates $k(T)$ cannot be used to accurately model non-equilibrium problems. The challenges of modeling non-equilibrium gas-phase chemical reactions are exemplified by hypersonic reentry into the earth's atmosphere (Figure 1) and other planetary atmospheres. For instance, nitrogen, which behaves as an inert gas in many processes, becomes chemically active under the high-temperature conditions of hypersonic reentry (~10,000 degrees). Atmospheric chemical reactions during hypersonic reentry are dominated by dissociation of molecular species and exchange reactions involving diatomic molecules and single

atoms. Ionization may also occur at higher temperatures.

Modeling chemical reactions at the extreme conditions of upper-atmosphere hypersonic flow has been very important from the Apollo era to the present because heat-absorbing endothermic chemical reactions can reduce heat transfer to the spacecraft. However, an in-depth understanding of the physical and chemical processes that take place in the flow field still remains elusive. The main reason for this is the difficulty in accurately measuring internal-energy-state-specific chemical reaction rates to validate theoretical models in the temperature range of interest. To avoid the inaccuracy of empirical Arrhenius-type chemical-reaction rates, new methods are being developed. The Direct Simulation Monte Carlo (DSMC) method of Bird (Reference 1), a molecular-gas-dynamics technique that tracks individual molecules as they move and collide, simulates gas flows

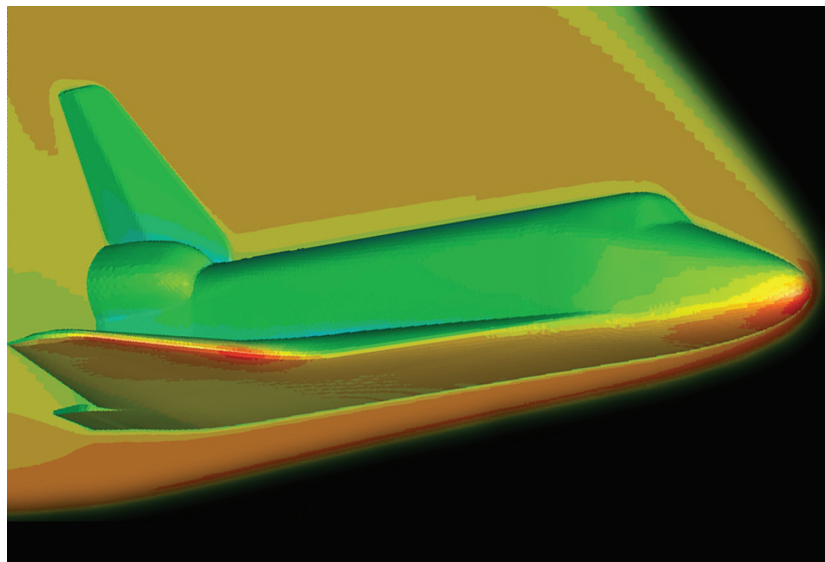


Figure 1: Simulation of the heating on the Space Shuttle as it enters the earth's atmosphere.



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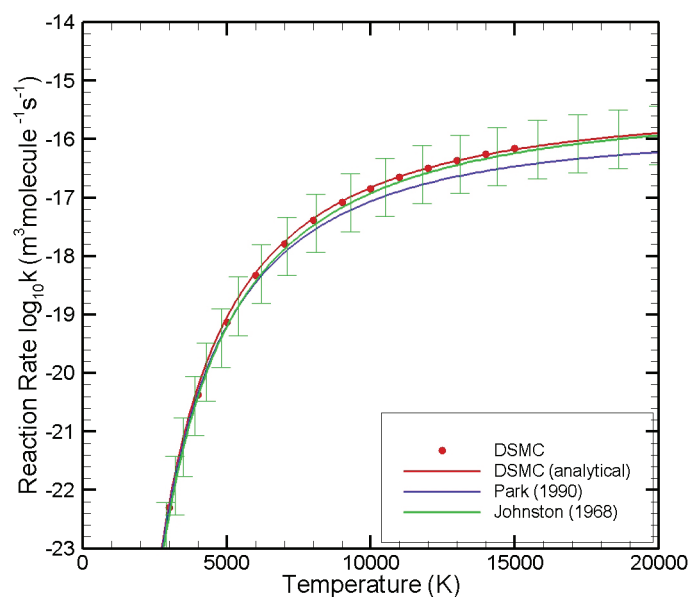


Figure 2: Comparison between predicted and measured equilibrium reaction rates for oxygen dissociation.

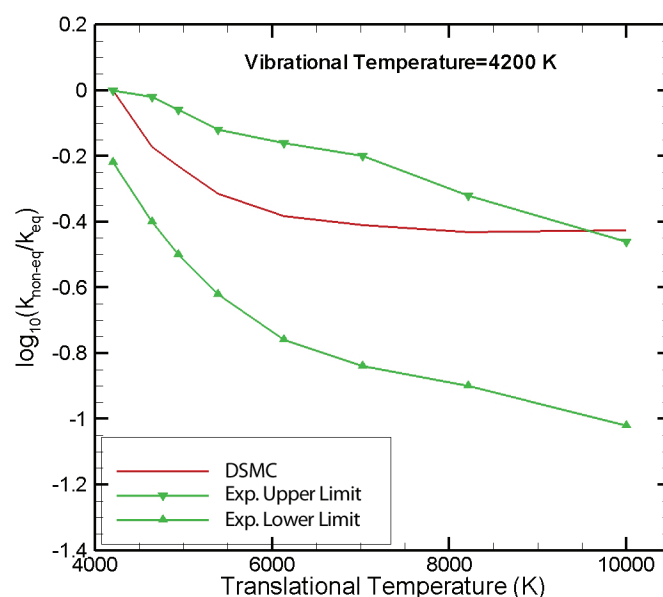


Figure 3: Comparison between predicted and measured non-equilibrium reaction rates for oxygen dissociation.

at the molecular level using kinetic-theory considerations and thus treats non-equilibrium gas behavior accurately. DSMC treats molecular collisions using stochastic rather than deterministic procedures to achieve greater computational efficiency.

Bird recently proposed a set of molecular-level “quantum-kinetic” chemistry models based solely on fundamental properties of two colliding molecules: their total collision energy, their quantized vibrational energy levels, and their molecular dissociation energies. These models link chemical-reaction cross-sections to the energy-exchange process and the probability of transition between vibrational energy states. These models apply directly to dissociation and endothermic exchange reactions. The energy-exchange procedures and the principle of microscopic reversibility are then used to derive models for the reverse situations: recombination and exothermic exchange reactions. These models do not require any macroscopic rate information, and they function by balancing the fluxes into and out of each state, thus satisfying microscopic reversibility.

At Sandia (References 2,3), this set of models was extended and refined for the dissociation of molecular oxygen under equilibrium (Figure 2) and non-equilibrium (Figure 3) conditions, and the resulting reaction rates are in good agreement with the best available measured or extrapolated reaction data. The experimental uncertainty of the measurements, typically one order of magnitude or greater, and the idealizations of the models do not allow

for an unequivocal assessment through these comparisons. However, the reaction-rate data and the DSMC predictions are always within one order of magnitude. This level of agreement is a source of optimism concerning the ability of the models to predict non-equilibrium reaction rates.

One of the most important features of this type of model is that it models chemically reacting flows from first principles, not only without knowledge of the macroscopic reaction rates but also without prior knowledge of which reactions will occur. As a result of their generality and flexibility, these models are currently being evaluated for reactions involving combustion, plasmas, complex molecules, and entry into other planetary atmospheres.

References

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3. Gallis, M. A., Bond, R. B., and Torczynski, J. R., Assessment of Collision-Energy-Based Models for Atmospheric-Species Reactions in Hypersonic Flows, *Journal of Thermophysics and Heat Transfer*, **24**, 241-253, 2010.